Problem Set 11 - 7.2, 7.5, 7.9, 7.10, 7.13, 7.16

7.2a. In order to see what order our reaction is, we will compare the data at hand to reaction mechanisms (rate equations) that we know. Since we have half life data, we want to compare to that. For first order reactions, (you can see how this equation is derived in problem 7.10a)

$$\ln\left(\frac{\frac{1}{2}c_0}{c_0}\right) = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

This tells us that the half life for first order reactions is independent of concentration, which clearly isn't the case for the data at hand. What about a second order reactions?

$$\frac{1}{\frac{1}{2}c_0} - \frac{1}{c_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{kc_0} \propto {c_0}^{-1}$$

In other words, doubling the initial concentration halves the half-life. Since this is what we observe, it is a plausible hypothesis for the mechanism.

b. Using the half-life equation for a second order reaction that we derived above,

$$t_{1/2} = \frac{1}{kc_0} \rightarrow k = \frac{1}{c_0 t_{1/2}} = \frac{1}{(0.0050\,\mathrm{M})(2000\,\mathrm{s})} = 0.1\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

You get the same answer if you use the other trial, where $c_0 = 0.0100\,\mathrm{M}$ and $t_{1/2} = 1000\,\mathrm{s}$.

c. We derived the integrated rate equation in (a) for a second order reaction, and the value for the rate constant $k = 0.1\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ that we derived in (b). For the case of $c_0 = 0.0100\,\mathrm{M}$,

$$t = \frac{1}{k}\left(\frac{1}{c} - \frac{1}{c_0}\right) = \frac{1}{0.1\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}}\left(\frac{1}{0.0025\,\mathrm{M}} - \frac{1}{0.01000\,\mathrm{M}}\right) = 3000\,\mathrm{s}$$

We could do the same thing for the case of $c_0 = 0.0050\,\mathrm{M}$, but we don't have to, as the answer is already given to us. Half of 0.0050 M **is** 0.0025 M, and we are told that the half life is 2000 s.

d. Since this is a second order reaction, the most obvious mechanisms are:

$$-\frac{\mathrm{d}\left[\mathrm{OH}^-\right]}{\mathrm{d}t} = k\left[\mathrm{OH}^-\right][\mathrm{CH_3COOC_2H_5}]$$

or

$$-\frac{\mathrm{d}\left[\mathrm{OH}^-\right]}{\mathrm{d}t} = k\left[\mathrm{OH}^-\right]^2$$

or

$$-\frac{\mathrm{d}\left[\mathrm{OH}^-\right]}{\mathrm{d}t} = k[\mathrm{CH_3COOC_2H_5}]^2$$

or even something like

$$-\frac{\mathrm{d}\left[\mathrm{OH}^-\right]}{\mathrm{d}t} = k\left[\mathrm{OH}^-\right]^{2\sin^2\theta}[\mathrm{CH_3COOC_2H_5}]^{2\cos^2\theta}\ ; 0 \le \theta \le 2\pi$$

e. The way to do this is by varying the concentration of one reactant without changing the other (and you might also consider setting the concentration of the fixed reactant very high so that it is effectively constant). You will do something like this in problem 7.5.

7.5a. The initial rate is $\nu_0 = k[A]^a[B]^b$. If doubling the initial concentration of A quadruples the initial rate, then the reaction must be second order with respect to $[A]$ (i.e., $a = 2$).

b. Likewise, if doubling the initial concentration of B does nothing to the rate, then the reaction must be zeroth order with respect to $[B]$ (i.e., $b = 0$).

c. From parts a and b, the rate expression must be

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = k[A]^2$$

d. From c, we know that the rate of the reaction is $\nu = k[A]^2$. To find the rate constant, k, we merely rearrange and substitute in the data in the table, i.e.,

$$k = \frac{\nu}{[A]^2} = \frac{1.0 \times 10^{-3}\,\mathrm{M\,s^{-1}}}{(1.0\,\mathrm{M})^2} = 1.0 \times 10^{-3}\,\mathrm{M^{-1}\,s^{-1}}$$

e. We know from the rate expression that two A molecules have to interact. Furthermore, since the reaction is zeroth order with respect to B, the reaction of with the B molecule must take essentially no time at all compared to the intial reaction of the two A's. One possible mechanism would be $A + A \rightarrow A_2^*$ (A collides with another A to form an activated complex) which must be a slow step, because, for example, there is a high barrier for the reaction so few molecules have enough kinetic energy at a given temperature to get over it. Then $A_2^* + B \rightarrow C + D + A$, occurs quickly, and the extra A molecule from the activated complex is returned so that the stoichiometric equation ($A + B \rightarrow C + D$) is obeyed. Of course the actual reaction might be more complicated than this, but Occam's razor is not just for shaving with.

7.9a We are asked to consider the reaction 2CGTGAATTCGCC $\rightleftharpoons$ *Duplex*, and given a set of kinetic data on the forward and backward rates k_1 and k_{-1}, respectively. To find the activation energy, E_a, consider the Arrhenius equation,

$$k = A\,\mathrm{Exp}\left[-\mathrm{E_a/RT}\right]$$

Since we don't know (or need to know) the value of A, the easiest thing to do is form a ratio that will cancel it out:

$$\ln\frac{k_2}{k_1} = \ln\left(\frac{A\,\mathrm{Exp}\left[-\mathrm{E_a/RT_2}\right]}{A\,\mathrm{Exp}\left[-\mathrm{E_a/RT_1}\right]}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_a = R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1}\ln\frac{k_2}{k_1}$$

where k_i is the rate constant at temperature T_i. I've massaged it into this form, because I'll just have a spreadsheet program calculate E_a from successive data points. If you're doing this without a spreadsheet, you can graph $\ln k$ versus $1/T$ and find the slope of the line, either through inspection, or with a linear regression.

To calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$, we need to consider Eyring's transition state theory equation,

$$k = \frac{k_B T}{h}\,\mathrm{Exp}\left[-\Delta\mathrm{G}^\ddagger/\mathrm{RT}\right]$$

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta G^\ddagger}{RT}$$

$$\Delta G^\ddagger = -RT\ln\left(\frac{kh}{k_B T}\right)$$

That's great, but we want to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$. One way to do this would be to plot $\Delta G^\ddagger$ versus T. The slope will be $-\Delta S^\ddagger$, and the intercept will be $\Delta H^\ddagger$. But graphing is tedious! Instead,

$$\Delta G^\ddagger{}_1 - \Delta G^\ddagger{}_2 = \left(\Delta H^\ddagger - T_1\Delta S^\ddagger\right) - \left(\Delta H^\ddagger - T_2\Delta S^\ddagger\right) = (T_2 - T_1)\,\Delta S^\ddagger$$

(Where we have made the implicit assumption that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are independent of temperature.) Then,

$$\Delta S^\ddagger = -\frac{\Delta G^\ddagger{}_2 - \Delta G^\ddagger{}_1}{T_2 - T_1}$$

and then

$$\Delta H^{\ddagger} = \Delta G^{\ddagger} + T\Delta S^{\ddagger}$$

I calculated these using a spreadsheet, and have tabulated them below

$T/^{\circ}\mathrm{C}$	T/K	k_1	$E_a/(\mathrm{kJ/mol})$	$\Delta G^{\ddagger}/(\mathrm{kJ/mol})$	$\Delta S^{\ddagger}/(\mathrm{J/mol\,K})$	$\Delta H^{\ddagger}/(\mathrm{kJ/mol})$
31.8	304.8	0.80	110	75.3	104	107
36.8	309.8	2.3	166	73.8	289	163
41.8	314.8	3.5	68.1	74.0	-26.9	65.5
46.7	319.7	6.0	92.1	73.7	49.1	89.4
		Average:	109	74.2	104	106

$T/^{\circ}\mathrm{C}$	T/K	k_{-1}	$E_a/(\mathrm{kJ/mol})$	$\Delta G^{\ddagger}/(\mathrm{kJ/mol})$	$\Delta S^{\ddagger}/(\mathrm{J/mol\,K})$	$\Delta H^{\ddagger}/(\mathrm{kJ/mol})$
31.8	304.8	1.00	243	74.7	543	240
36.8	309.8	3.20	183	73.0	346	180
41.8	314.8	15.4	254	70.1	579	252
46.7	319.7	87.0	296	66.6	708	293
		Average:	244	71.1	544	241

b. The difference between the backwards and forwards reaction $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ should determine the overall ΔH° and ΔS°, i.e., $\Delta H^{\circ} = \Delta H^{\ddagger}{}_{rev} - \Delta H^{\ddagger}{}_{fwd}$ and $\Delta S^{\circ} = \Delta S^{\ddagger}{}_{rev} - \Delta S^{\ddagger}{}_{fwd}$. They are tabulated below in kJ/mol for $\Delta H^{\ddagger}$ and J/mol K for $\Delta S^{\ddagger}$.

$\Delta H^{\ddagger}{}_{fwd}$	$\Delta H^{\ddagger}{}_{rev}$	ΔH°
107	240	-133
163	180	-16.8
65.5	252	-187
89.4	293	-204
	Average:	-135

$\Delta S^{\ddagger}{}_{fwd}$	$\Delta S^{\ddagger}{}_{rev}$	ΔS°
104	543	-439
289	346	-57
-26.9	579	-605
49.1	708	-659
	Average:	-440

c. Forming an extra Watson-Crick base pair will stabilize the product, that is, make the activation energy for the reverse reaction larger (and do nothing to E_a for the forward reaction). You can derive from,

$$E_a = RT^2 \frac{\partial\, \mathrm{ln} k}{\partial T}$$

and

$$k = \frac{k_B T}{h}\, \mathrm{Exp}\left[-(\Delta \mathrm{H}^{\ddagger} - \mathrm{T}\Delta \mathrm{S}^{\ddagger})/\mathrm{RT}\right]$$

that (I won't show it here, but it's pretty easy to do on your own, as an exercise for the reader)

$$E_a = \Delta H^{\ddagger} + RT$$

In other words, increasing E_a for the reverse reaction will make $\Delta H^{\ddagger}$ for the reaction increase as well.
7.10 For the reaction $A + B \to C$, we are told that after 1 hour, 90% of A is reacted, i.e., that $[A]_{1\,hr} = 0.10[A]_0$. Having established this, we proceed with the problem.

a. For first order in A and zeroth order in B,

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]$$

$$\int \frac{\mathrm{d}[A]}{[A]} = -k \int \mathrm{d}t = \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$-\frac{\ln\left(\frac{0.10[A]_0}{[A]_0}\right)}{1\,\mathrm{hr}} = k = 2.3\,\mathrm{hr}^{-1}$$

Using this value for k, we can return to our original integrated rate expression, and we see that after $t = 2\,\mathrm{hr}$,

$$\frac{[A]}{[A]_0} = \mathrm{Exp}\left[-\mathrm{kt}\right] = \mathrm{Exp}\left[(2.3\,\mathrm{hr}^{-1})(2\,\mathrm{hr})\right] = 0.01$$

Therefore 1% is unreacted at the end of 2 hours.
b. For a reaction first order in both A and B,

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B]$$

However, we are told that the reactants are present in the same concentration (equal volumes of equimolar solutions), so our equation simplifies to:

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^2$$

Integrating,

$$-\int \frac{\mathrm{d}[A]}{[A]^2} = \int k\mathrm{d}t = \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) = \frac{1}{(1\,\mathrm{hr})}\left(\frac{1}{0.1[A]_0} - \frac{1}{[A]_0}\right) = 9\,\mathrm{hr}^{-1}{[A]_0}^{-1}$$

And, as in part a, using this value of k and our integrated rate equation, we find

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$[A] = \left(kt + \frac{1}{[A]_0}\right)^{-1} = \left((9\,\mathrm{hr}^{-1}{[A]_0}^{-1})(2\,\mathrm{hr}) + \frac{1}{[A]_0}\right)^{-1} = 0.053[A]_0$$

So 5.3% of the A is remaining at the end of 2 hr.
c. Again, same procedure, just a different equation to integrate. The reaction is zeroth order in A and B, so

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k \;\rightarrow\; \int \mathrm{d}[A] = -k \int \mathrm{d}t = [A] - [A]_0 = -kt$$

Rearranging for the rate constant,

$$k = -\left(\frac{[A] - [A]_0}{t}\right) = -\left(\frac{0.10[A]_0 - [A]_0}{1\,\mathrm{hr}}\right) = 0.9[A]_0\,\mathrm{hr}^{-1}$$

Then rearranging our integrated rate equation,

$$[A] = [A]_0 - kt = [A]_0 - (0.9[A]_0\,\mathrm{hr}^{-1})(2\,\mathrm{hr}) = -0.8[A]_0$$

But this is impossible, as “negative concentration” is unphysical. So the conclusion is that either we ran out of reactants at around 1.1 hr (and so the reaction stopped before we could get to the 2 hr mark) or else the kinetics changed in the limit of low concentration.

d. For the case of a mechanism first order in A and half-order in B,

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A][B]^{1/2} = k[A]^{3/2}$$

by the same argument that we made in part b. Integrating this equation (do you sense a pattern here?),

$$-\int \frac{\mathrm{d}[A]}{[A]^{3/2}} = \int k\mathrm{d}t = 2\left(\frac{1}{[A]^{1/2}} - \frac{1}{{[A]_0}^{1/2}}\right) = kt$$

Solving for the rate constant,

$$k = \frac{2}{t}\left(\frac{1}{[A]^{1/2}} - \frac{1}{{[A]_0}^{1/2}}\right) = \frac{2}{(1\,\mathrm{hr})}\left(\frac{1}{(0.1[A]_0)^{1/2}} - \frac{1}{{[A]_0}^{1/2}}\right) = 4.3\,\mathrm{hr}^{-1}{[A]_0}^{-1/2}$$

And (finally) solving for $[A]$ at $t = 2\,\mathrm{hr}$,

$$[A]^{1/2} = \left(\frac{kt}{2} + \frac{1}{{[A]_0}^{1/2}}\right)^{-1}$$

$$[A] = \left(\frac{kt}{2} + \frac{1}{{[A]_0}^{1/2}}\right)^{-2} = \left(\frac{(4.3\,\mathrm{hr}^{-1}{[A]_0}^{-1/2})(2\,\mathrm{hr})}{2} + \frac{1}{{[A]_0}^{1/2}}\right)^{-2} = 0.036$$

So about 3.6% is remaining after two hours.

7.13 We are told that the half life of $^3_1$H is $t_{1/2} = 12.5\,\mathrm{yr}$, and that the reaction is first order in $^3_1$H only. The rate equation is,

$$-\frac{\mathrm{d}[^3_1\mathrm{H}]}{\mathrm{d}t} = k[^3_1\mathrm{H}]$$

Which is integrated to,

$$\int \frac{\mathrm{d}[^3_1\mathrm{H}]}{[^3_1\mathrm{H}]} = -k\int \mathrm{d}t = \ln\left(\frac{[^3_1\mathrm{H}]}{[^3_1\mathrm{H}]_0}\right) = -kt$$

Solving for k using the half life data,

$$k = \frac{\ln\left(\frac{[^3_1\mathrm{H}]}{[^3_1\mathrm{H}]_0}\right)}{t_{1/2}} = \frac{\ln 2}{12.5\,\mathrm{yr}} = 0.0555\,\mathrm{yr}^{-1}$$

Using this value in our integrated rate equation,

$$t = -\frac{\ln\left(\frac{[^3_1\mathrm{H}]}{[^3_1\mathrm{H}]_0}\right)}{k} = -\frac{\ln\left(\frac{0.20[^3_1\mathrm{H}]_0}{[^3_1\mathrm{H}]_0}\right)}{0.0555\,\mathrm{yr}^{-1}} = 29.0\,\mathrm{yr}$$

(The astute reader will seee that this problem is exactly the same as 7.10a.) So the question now becomes: Was $(2001 - 29) = 1972$ a good year? But since this is not a oenology class, we won’t answer that question. As an exercise to the reader, you might try the inverse problem: try finding the amount of $^3_1$H left in wine that was bottle the year you were born.

7.16a. We are told that U is produced by a zeroth order mechanism with rate constant k_0 and degraded by a first order mechanism with rate constant k_1. Clearly, the rate expression is,

$$\frac{\mathrm{d}[\mathrm{U}]}{\mathrm{d}t} = k_0 - k_1[\mathrm{U}]$$

b. To solve this problem, all we have to do is integrate the rate expression we derived in part a. The linear differential equation

$$\frac{\mathrm{d}y}{\mathrm{d}x} + P(x)y = Q(x)$$

has the solution

$$y = e^{-\int P(x)\mathrm{d}x}\left[\int Q(x)e^{\int P(x)\mathrm{d}x}\mathrm{d}x + c\right]$$

All we need to do is rearrange our rate expression from part a into the form,

$$\frac{\mathrm{d[U]}}{\mathrm{d}t} + k_1[\mathrm{U}] = k_0$$

to see that $y = [\mathrm{U}]$, $x = t$, $P(x) = k_1$, and $Q(x) = k_0$. Then,

$$[\mathrm{U}] = \left(e^{-\int_0^t k_1 \mathrm{d}t}\right)\left[\int_0^t k_0 e^{\int_0^k k_1 \mathrm{d}t}\mathrm{d}t + c\right]$$

$$[\mathrm{U}] = \left(e^{-k_1 t + 0}\right)\left[k_0 \int_0^t e^{k_1 t + 0}\mathrm{d}t + c\right]$$

$$[\mathrm{U}] = \frac{k_0}{k_1}e^{-k_1 t}\left(e^{k_1 t} - 1 + c\right) = \frac{k_0}{k_1}\left(1 - e^{-k_1 t} + c\right)$$

but since $[\mathrm{U}(t = 0)] = 0$, then $c = 0$, so

$$[\mathrm{U}] = \frac{k_0}{k_1}\left(1 - e^{-k_1 t}\right)$$

If you want to take the easy way out, you can use the answer they give you, and take the derivative with respect to time to see if it gives you the same answer; strictly speaking, you are only asked to verify the answer, not derive it. But calculus is fun!

c. We are told that $k_0 = 1.00\,\mathrm{nM\,s^{-1}}$ and that $t_{1/2} = 0.500\,\mathrm{hr}$ for the degradation reaction. We derived earlier in this problem set that for a first order reaction, $t_{1/2} = (\ln 2)/k_1$, so

$$k_1 = \frac{\ln 2}{t_{1/2}} = \left(\frac{\ln 2}{0.500\,\mathrm{hr}}\right)\left(\frac{1\,\mathrm{hr}}{3600\,\mathrm{s}}\right) = 3.86 \times 10^{-4}\,\mathrm{s^{-1}}$$

We know from calculus that extrema occur when

$$\frac{\mathrm{d[U]}}{\mathrm{d}t} = k_0 - k_1[\mathrm{U}] = 0$$

which is particularly easy to rearrange, in order to find that the maximum concentration is

$$[\mathrm{U}] = \frac{k_0}{k_1} = \frac{1.00\,\mathrm{nM\,s^{-1}}}{3.86 \times 10^{-4}\,\mathrm{s^{-1}}} = 2.59 \times 10^3\,\mathrm{nM} = 2.59\mu\,\mathrm{M}$$

When does it occur? Using the integrated rate expression for [U] we derived in part b,

$$\ln\left(1 - \frac{k_1}{k_0}[\mathrm{U}]\right) = -k_1 t$$

$$t = -\frac{1}{k_1}\ln\left(1 - \frac{k_1}{k_0}[\mathrm{U}]\right) = -\frac{1}{3.86 \times 10^{-4}\,\mathrm{s^{-1}}}\ln\left[1 - \frac{3.86 \times 10^{-4}\,\mathrm{s^{-1}}}{1.00\,\mathrm{nM\,s^{-1}}}(2.59 \times 10^3\,\mathrm{nM})\right] = 2.13{\times}10^4\,\mathrm{s} = 5.94\,\mathrm{hr} \blacksquare$$

However, this is **wrong**; in fact, it is due to a round off error. If you think about it for a minute,

$$t = \frac{-1}{k}\ln\left(1 - \frac{k_1}{k_0}[\mathrm{U}]\right) = \frac{-1}{k}\ln\left(1 - \frac{k_1}{k_0}\frac{k_0}{k_1}\right) = \frac{-1}{k}\ln 0 = \infty$$

Therefore it takes an infinite time to reach the maximum concentration, because (and you'll see this if you graph it), [U] approaches the maximum asymtotically.

d. To reach $[\mathrm{U}] = 1.00\mu\,\mathrm{M}$, we simply do the same as in b,

$$t = -\frac{1}{k_1}\ln\left(1 - \frac{k_1}{k_0}[\mathrm{U}]\right) = -\frac{1}{3.86\times10^{-4}\,\mathrm{s}^{-1}}\ln\left[1 - \frac{3.86\times10^{-4}\,\mathrm{s}^{-1}}{1.00\,\mathrm{nM\,s}^{-1}}(1.00\times10^{3}\,\mathrm{nM})\right] = 1.26{\times}10^{3}\,\mathrm{s} = 0.351\,\mathrm{hr}$$

e. This calculation is exactly the same as d, but with $k_0 = 0.500\,\mathrm{nM\,s}^{-1}$, and it gives the solution $t = 3830\,\mathrm{s} = 1.06\,\mathrm{hr}$.

f. To find the smallest k_0 that will reach the $[\mathrm{U}] = 1.00\mu\,\mathrm{M}$ cut off necessary for cell replication, we need to consider the limit as $t \to \infty$,

$$\lim_{t\to\infty}[\mathrm{U}] = \frac{k_0}{k_1}\left(1 - e^{-k_1\infty}\right) = \frac{k_0}{k_1}$$

$$k_0 = k_1[\mathrm{U}] = (3.86\times10^{-4}s^{-1})(1.00\times10^{3}\,\mathrm{nM}) = 0.386\,\mathrm{nM\,s}^{-1}$$